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Effect of the secondary product of semi-solid phase Fenton on the flotability of electrode material from spent lithium-ion battery

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ABSTRACT

Fenton modified flotation is one of the effective ways to separate and recycle the electrode materials, $LiCoO_2$ and graphite, from spent lithium-ion batteries (LiBs). However, a satisfactory $LiCoO_2$ grade of flotation concentrate still could not be achieved after the Fenton modification. Comparison of its flotation results with the direct flotation and roasting modified flotation indicates the concentrate grade of $LiCoO_2$ after Fenton treatment only increased by 5%, reaching 60%, while that of the roasting flotation could be up to 90%. Analyses of surface morphology and chemical composition indicate that the newborn surface of the electrode particles are wrapped with an inorganic compound layer composed of $Fe(OH)_3$, which is the secondary product of semi-solid phase Fenton. The inorganic film results in a similar hydrophobicity and finally leads to the poor flotation results. Deducing from the reaction mechanism of Fenton, the enhancement of alkaline environment is a main reason for the precipitation of Fe^{3+} on the surface of particles. Therefore, an appropriate amount of hydrochloric acid (HCl) was added to react with precipitation, and the final concentrate grade reached 75%.

1. Introduction

Due to advantages of high energy density, no memory effect, low self-discharge rate, small size and light weight [1], rechargeable lithium-ion batteries (LiBs) have substituted nickel-cadmium (NiCd) batteries and nickel-metal hydride (NiMH) batteries as power sources for consumer electronics [2]. Moreover, LiBs are considered as the best energy source of pure electric vehicles(EVs) [3]. Great market demand directly contributed to a substantial increase in battery sales [4]. It is expected that the market value of LiBs is US $31.4 billion in 2015 and will up to US $53.7 billion in 2020 [5]. Nevertheless, the limitation of service live lead to the rapid growth of waste LiBs. These wastes are important secondary source of metals; to some extent, the metal grade is higher than that of natural ores or even concentrated ores [6]. On the other hand, the recovery of cobalt and nickel to re-create cathode materials can contribute to following savings: 45.3% in fossil fuels, 51.3% in natural resources, and 57.2% in nuclear energy demand [7]. The value of individual components is cathode materials($6101), copper($654), aluminum($103), graphite($170) and others($680) [8]. In addition, the price of raw cobalt continues to rise in recent years, which makes the recovery of cathode material become economically feasible [9].

Spent LiBs contain toxic and harmful waste [10–12]. If not properly handled, they will pollute the environment and endanger animals and human health. LiBs are composed of heavy metals (5%–20% cobalt, 5%–10% nickel, 5%–15% manganese), organic compounds(15%), and plastics(7%) [13]. Data indicates that there will be 1100 tons of heavy metals and 200 tons of toxic electrolyte penetrating out from 4000 tons of waste LiBs [7]. In addition, it is difficult to degrade some components of LiBs. This means if dropping into municipal waste landfill arbitrarily, spent LiBs may contaminate the soil and groundwater resources [13]. Therefore, it is necessary to emphasize that irresponsible disposal of waste LiBs would cause environmental pollution [14]. In recent years, governments regulate a more flexible recovery mechanism through legislation. For example, EU member states are required to achieve a minimum recovery rate of 15–25% before 2016 and cumulative recovery efficiency of 45–50% at least [13]. Accordingly, the recovery of batteries is welcomed, environmental friendly and beneficial to sustainable development.

Recycling methods of waste LiBs are mainly divided into physical methods and chemical methods. The physical processes include mechanical separation method, thermal treatment, mechanochemical method and dissolution processes [14]. The chemical processes include acid leaching, bioleaching, solvent extraction, chemical precipitation and electrochemical processes [15]. High treatment capacity and simple operation make the physical method be the best approach to recycle cathode materials in industrial production. Chemical treatment is the

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only way to recover precious metals with high purity. To some extent, physical method is the pretreatment of chemical processes. Selective combination of the two methods is the best solution. Zhang et al. [16] and Li et al. [17] considered that waste LiBs had obvious selectivity crushing behavior. After crushed, electrode materials are enriched in −0.075 mm size fraction, which are so called cobalt-enriched products. Electrode materials have high recovery value, so extensive studies focus on the cobalt-enriched product. $LiCoO_2$ belongs to hexagonal crystal system [18], with excellent layered structure and hydrophilic behavior. However, graphite is a nonpolar mineral, with low surface bonding energy and good hydrophobicity. The great difference in surface hydrophobicity makes flotation be a theoretically ideal method to separate $LiCoO_2$ and graphite. Jin et al. [19] and Li et al. [20] found that after crushed, both the surface of $LiCoO_2$ and graphite are covered by a layer of organic matter, whose component is about 5% PVDF, about 30% carbon black, and about 50% C—C/C—H structure. Similar surface composition decreases the differences in the surface properties, which ultimately results in poor flotation. Although moderate roasting can remove organic compound layer on the particle surface to improve flotation effect, harmful ingredients would volatilize and produce irritating gases, such as HF, P_2O_5, and aldehydes under high temperature circumstance [19]. There are serious environmental problems on roasting flotation in industrialization. He et al. [21] utilized semi-solid phase Fenton method to remove the organic plasma membrane on the surface of the particles. In this method, harmful components in the organic plasma membrane are oxidized to harmless inorganic salts, such as phosphate, carbonate and so on. This is an efficient and environmentally friendly solution to the problem of the adsorption of organic compound layer, which is also an important reason for restricting the cost and efficiency of hydrometallurgy and biochemical leaching [22–25]. However, the occurrence state of inorganic salts from Fenton and their effects on flotation have not been studied. In order to improve the Fenton flotation results, the above studies have focused on the composition and content of organic matter on the surface of the particles. But the research on the changes of inorganic materials on the particle surface before and after Fenton treatment is relatively rare. It is also necessary to supplement this lack of the research.

In this paper, the results of flotation with three treatment methods, namely direct flotation, Fenton modified flotation and roasting modified flotation, were analyzed and discussed. Scanning electron microscope (SEM) and field emission electron probe microanalyzer (FE-EPMA) were used to analyze the changes in the properties of inorganic substances on the particles surface before and after Fenton treatment. The formation mechanism of secondary product from the Fenton reaction was also revealed. The improved Fenton modified method was put forward to achieve the purpose of high efficiency and environmental protection.

2. Experiment

2.1. Experimental raw materials

100 pieces of spent lithium-ion batteries with the same manufacturer and model, were discharged in 5 wt% sodium chloride solution at room temperature for 48 h. Then they were taken out to dry naturally in a fume hood for 24 h. All batteries were manually disassembled and the electrode strips were taken out. The positive and negative electrode strips were broken to pass 0.074 mm sieve by the universal crusher, respectively. The crushed electrode materials, $LiCoO_2$ and graphite, were mixed with the mass ratio of 1:1 as the experimental raw material. With the help of the element analysis of X-ray fluorescence spectrometer (XRF, Bruker S8 Tiger, Germany), the $LiCoO_2$ grade of flotation concentrates were determined. The flow sheet of the preparation is shown in Fig. 1(a).

2.2. Fenton and roasting process

In advanced oxidation process of semi-solid phase Fenton, 0.8 mol/L H_2O_2 and 0.1 mol/L $FeSO_4 \cdot 7H_2O$ were mixed with a volume ratio of 15:1, and a solution whose molar ratio of H_2O_2 to Fe^{2+} is 120:1 was prepared. The experimental raw material was added with the liquid-solid ratio as 75:1. To more specific, firstly, 500 mL H_2O_2 was added in the beaker, and pH should be adjusted to 3. 33.3 mL $FeSO_4 \cdot 7H_2O$ and 7 g experimental material were added in sequence and stirred for 20 min. Finally, the material was filtered with plenty of deionized water rinsing and dried as flotation feed. The flow sheet of Fenton treatment is shown in Fig. 1(b).

Roasting oxidation process is relatively simply. About 1.00 g sample was weighed in each porcelain boat, being shaken to disperse, and they were put into muffle furnace. It was slowly heated up to 415 °C for 20 min. 20–50 porcelain boats can be roasted process at a time. The average ignition loss ratio of sample is 10%–15%.

2.3. Flotation experiment

Flotation experiments were performed in a 100 mL XFG flotation cell at room temperature. Pulp concentration, impeller speed, collector and frother were 40 g/L, 1960 rpm, 300 g/t kerosene and 150 g/t 2-Octanol, respectively. The slurry was stirred for 1 min after each addition of the agent. The time for skimming off the froth was 3 min. After filtration and drying, the flotation recovery rate was calculated by the texts of XRF. The flow sheet of flotation is shown in Fig. 1(c).

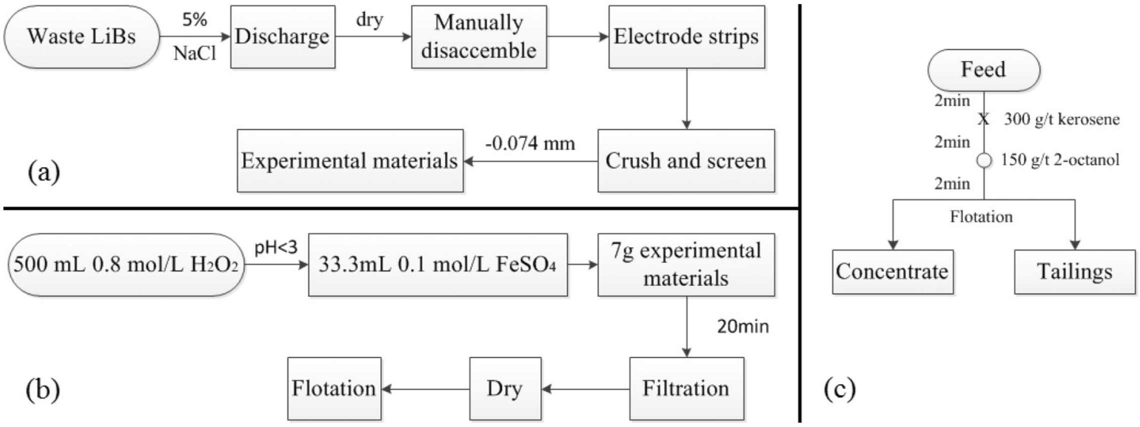

Fig. 1. Flow sheets of experimental methods (a. the preparation of experimental materials; b. Fenton treatment; c. flotation).